

Role of Rhodium in RhPt catalysts for ammonia oxidation revealed by operando STM and AP-XPS

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Motivated to develop a future abatement technology dedicated to eliminate NO_x release from diesel-powered engines, we research ammonia oxidation catalysts. Our latest results show that Rh-promoted Pt/Al₂O₃ is a promising catalyst to tackle this challenge. To understand the fundamentals of the ammonia oxidation over RhPt/Al₂O₃ we reproduced this catalyst with two complementary model surfaces RhPt/Pt(111) and RhPt/Al₂O₃/NiAl(110). Both surfaces model commercial catalyst to different degrees of complexity: the former allows for precise control of cluster morphology (triangular vs hexagonal, single or double layered) and can be greatly affected by temperature (Fig. 1a-b),[1] while the latter offers fewer variations in morphology (spherical nanoparticles) (Fig. 1c), however excludes active contribution from the Pt substrate, also allowing study metal (RhPt) – support (Al₂O₃) interactions.

The ammonia oxidation reaction is controlled by a) composition and morphology of the catalytic surface; b) presence of O- and N- surface species; and c) oxidation state of the catalyst active surface. Therefore, we established structure-reactivity relationship by obtaining series of operando high-pressure STM and ambient-pressure XPS measurements following intermediate temperature oxidation of ammonia over RhPt clusters on Pt(111) and Al₂O₃/Ni(110) at commercially relevant conditions (1mbar-2bar NH₃+O₂, RT-250 °C).[2]

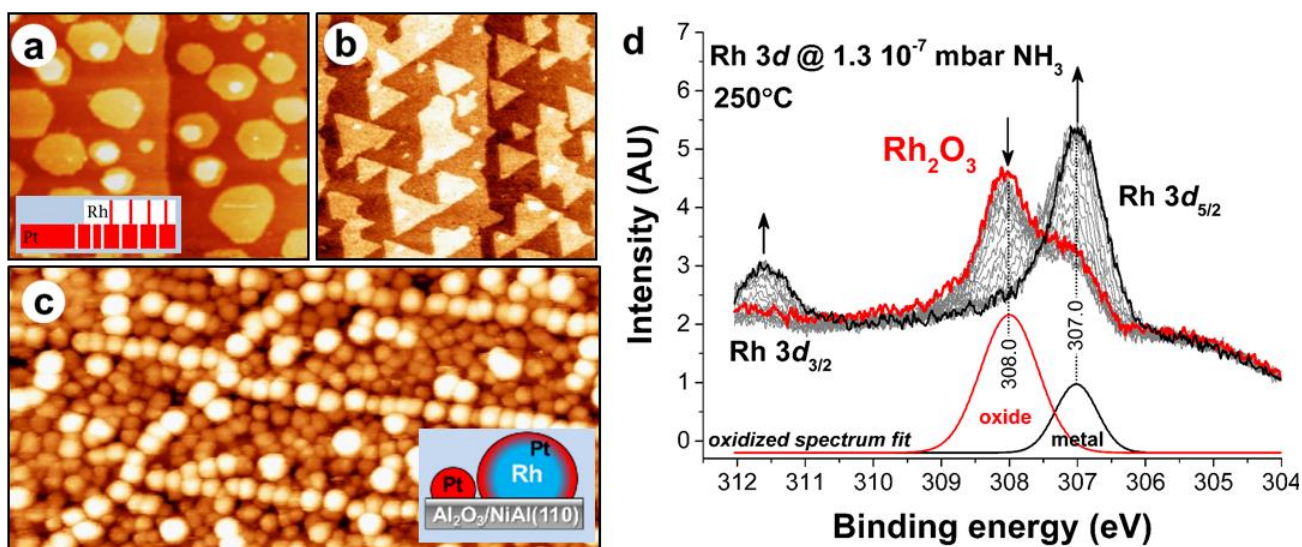


Figure 1a-c STM topography images of RhPt bimetallic surfaces showing variety of possible morphologies (hexagons, triangles and nanoparticles): **a)** 0.5 ML Rh deposited on Pt(111) at 23°C, and annealed to 325°C to promote alloying of Rh and Pt. Image size 60x60nm, U_t -0.5V, I_t 0.2nA. **b)** 0.5 ML Rh deposited on Pt(111) at 275°C showing large triangular clusters, image size 115x130nm. **c)** PtRh bimetallic surfaces obtained by sequential deposition of 0.3 ML Rh + 0.3 ML Pt onto Al₂O₃/NiAl(110). Image size 38x80nm, U_t -3V, I_t 0.2nA. **d)** Ambient pressure XPS spectra corresponding to the reduction of Rh oxide during dosing of 1.3 10⁻⁷ mbar NH₃ at 250°C over RhPt/Pt(111). As prepared, Rh is in its metallic state (BE 307.0 eV), oxidation at 0.5 mbar O₂ and RT-250°C creates an oxide layer (BE 308.0 eV). Gas exchange from O₂ to NH₃ induces rapid depletion of oxide at the surface, reverting Rh to its original metallic state.

References:

- [1] Jian Zheng, Oleksii Ivashenko, Helmer Fjellvåg, Irene M.N. Groot, Anja O. Sjøstad, submitted to JPCC
- [2] Oleksii Ivashenko, Jian Zheng, Niclas Johansson, Irene M.N. Groot, Joachim Schnadt, Anja O. Sjøstad, in preparation